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Complexes of a novel *N*-(diisopropxythiophosphoryl)thiourea derivative of 1,4,8,11-tetraazacyclotetradecane with Na^+, K^+ and $Cu(PPh_3)_2^+$ cations

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Abstract

The reaction between 1,4,8,11-tetraazacyclotetradecane (cyclam) and *O*,*O*′-diisopropyl-isothiocyanatothiophosphoric acid $(i\mathrm{PrO})_2\mathrm{P(S)NCS}$ gives the tetra-functional thiourea H_4L with four $\mathrm{C(S)NHP(S)(OPr}i)_2$ groups attached to the intracyclic nitrogen atoms. The tetra-substituted product has been obtained in the solid state, while partial dissociation with elimination of isothiocyanate $(i\mathrm{PrO})_2\mathrm{P(S)NCS}$ takes place in CCl_4 and $CDCl_3$ solutions. Deprotonation of the exocyclic groups prevents the dissociation, and alkali metal salts of M_4L formula ($M = Na^+$, K^+) were obtained by treatment with MOH. The potassium salt K_4L was used to synthesize the Cu(I) complex $[\{Cu(PPh_3)_2\}_4L]$ by reaction with $Cu(PPh_3)_3I$.

Keywords: Azacrown ether; Chelate; Cyclam; Macrocycle; Supramolecular chemistry; Thiourea

1. Introduction

Major interest is devoted to macrocycles bearing pendant complexing groups, mainly due to the increase in selectivity and efficacy in metal ion binding [1], and also for studying the interactions between various complexing groups within a ligand molecule. The pendant groups are capable of participating in the coordination to the metal ions, connected by the macrocyclic cavity, and allow the properties of the bound metal ions to be changed, while the metal ions, in turn, affect the reactivity of the lateral groups [2]. Ligands containing pendant groups, operating irrespective of a macrocycle, are widely used in the studies on the properties of heteronuclear complexes [3].

Currently the chemistry of functionalized macrocycles continues to develop intensively. These molecules play an important role in the processes of molecular recognition of organic compounds [4,5]. Complexes of modified aza-crowns are useful as agents for the selective binding of actinides [6]. Great attention is given to functionalized macrocycles and their complexes for the process of binding of anions and ionic pairs [7].

Convenient and effective means of introducing pendant groups into the structure of aza-macrocycles are the reactions with the participation of the intracyclic nitrogen atom [1,5,8]. In our opinion, the addition reaction of macrocyclic amines to activate cumulenes, such as isocyanates and isothiocyanates of (thio)phosphoric acids, are very useful. Our earlier works have discussed aza-crown ether derivatives, containing exocyclic *N*-(thio)phosphorylated urea and thiourea moieties $RC(X)NHP(Y)(OAlk)_2$ ($R = R'_2N$, R′NH; X, Y = O, S) [9], and their complexes with transition metal ions: Cu(I) [10], Ni(II) [11] and Co(II) [12].

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